AFRL-RX-WP-JA-2016-0243

OPTICAL SENSITIZING OF PHOTOREFRACTIVE Sn2P2S6 WITH CW AND PULSED PRE-EXPOSURE (PREPRINT)

Dean R. Evans, Sergey A. Basuna, and Carl M. Liebig
AFRL/RX

Sergey A. Basun
Azimuth Corporation

Larry E. Halliburton
West Virginia University

Yaroslav Skrypkad, Alexandr M. Shumelyukd, and Serguey G. Odoulovd
Natiional Academy of Sciences, Kiev

21 MAY 2015
Interim Report

AIR FORCE RESEARCH LABORATORY
MATERIALS AND MANUFACTURING DIRECTORATE
WRIGHT-PATTERSON AIR FORCE BASE, OH 45433-7750
AIR FORCE MATERIEL COMMAND
UNITED STATES AIR FORCE

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YY)*	2. REPORT TYPE	3. DATES COVERED *(From - To)*
21 May 2015	Interim	1 December 2009 – 21 April 2015

4. TITLE AND SUBTITLE
OPTICAL SENSITIZING OF PHOTOREFRACTIVE Sn2P2S6 WITH CW AND PULSED PRE-EXPOSURE (PREPRINT)

5a. CONTRACT NUMBER
FA8650-09-D-5434-0011

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER
63112F

6. AUTHOR(S)
1) Dean R. Evans, Sergey A. Basuna, and Carl M. Liebig – AFRL/RX
2) Sergey A. Basun- Azimuth Corp
(continued on pg. 2)

5d. PROJECT NUMBER
2001

5e. TASK NUMBER 0011

5f. WORK UNIT NUMBER
X08M

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
1) AFRL/RX
Wright_Patterson AFB, OH 45433-7750
2) Azimuth Corporation
4134 Linden Avenue, Suite 300, Dayton, OH 45432
(continued on page 2)

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Air Force Research Laboratory
Materials and Manufacturing Directorate
Wright-Patterson Air Force Base, OH 45433-7750
Air Force Materiel Command
United States Air Force

10. SPONSORING/MONITORING AGENCY ACRONYM(S)
AFRL/RXAP

11. SPONSORING/MONITORING AGENCY REPORT NUMBER(S)
AFRL-RX-WP-JA-2016-0243

12. DISTRIBUTION/AVAILABILITY STATEMENT
Distribution Statement A. Approved for public release: distribution unlimited.

13. SUPPLEMENTARY NOTES
PA Case Number: 88ABW-2015-2480; Clearance Date: 21 May 2015. This document contains colorThe U.S. Government is joint author of the work and has the right to use, modify, reproduce, release, perform, display, or disclose the work.

14. ABSTRACT *(Maximum 200 words)*
Pre-exposure of Sn2P2S6 to visible light gives rise to a temporary increase of the effective trap density and therefore improves the photorefractive response. With cw pre-exposure and nanosecond pulse pre-exposure we study temporal dynamics of the Sn2P2S6 sample transmission to reveal a sequence of processes that result in a desirable sensitization.

15. SUBJECT TERMS
Low-symmetry photorefractive crystals, nonlinear absorption, optical sensitizing

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT:	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON (Monitor)
a. REPORT	b. ABSTRACT	c. THIS PAGE			Byron Edmonds
Unclassified	Unclassified	Unclassified	SAR	6	19b. TELEPHONE NUMBER *(Include Area Code)* (937) 255-9638

REPORT DOCUMENTATION PAGE Cont'd

6. AUTHOR(S)

3) Larry E. Hallliburton – West Virginia University

4) Yaroslav Skrypkad, Alexandr M. Shumelyukd, and Serguey G. Odoulovd – National Academy of Sciences, Kiev

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

3) West Virginia University, 1500 University Ave
Stewart Hall, Morgantown, WV 26506

4) Institute of Physics, National Academy of Sciences,
46 Science Ave,

OPTICAL SENSITIZING OF PHOTOREFRACTIVE $Sn_2P_2S_6$ WITH CW AND PULSED PRE-EXPOSURE

Dean R. Evans*[a], Sergey A. Basun[a,b], Carl M. Liebig[a], Larry E. Halliburton[c], Yaroslav Skrypka[d], Alexandr M. Shumelyuk[d], and Serguey G. Odoulov[d]

[a]Air Force Research Laboratory, Materials and Manufacturing Directorate, Wright-Patterson AFB, OH, 45433, USA

[b]Azimuth Corporation, 4134 Linden Avenue, Suite 300, Dayton, OH 45432, USA

[c]Department of Physics, West Virginia University, Morgantown, West Virginia 26506, USA

[d]Institute of Physics, National Academy of Sciences, 46 Science Ave, 03650 Kyiv, Ukraine

ABSTRACT

Pre-exposure of $Sn_2P_2S_6$ to visible light gives rise to a temporary increase of the effective trap density and therefore improves the photorefractive response. With cw pre-exposure and nanosecond pulse pre-exposure we study temporal dynamics of the $Sn_2P_2S_6$ sample transmission to reveal a sequence of processes that result in a desirable sensitization.

Keywords: Low-symmetry photorefractive crystals, nonlinear absorption, optical sensitizing

The pre-illumination of $Sn_2P_2S_6$:Sb samples with cw light results in two distinct effects: time delayed transient photoinduced absorption (photo-chromism) [1], and transient photoinduced scattering (transient beam fanning) [2]. The second effect is a consequence of light induced enhancement of the photorefractive response. Both effects are well pronounced in crystals with 1% of Sb; a much smaller effect of sensitizing with considerably different lifetimes of secondary centers was observed in nominally undoped $Sn_2P_2S_6$, tellurium doped $Sn_2P_2S_6$:Te 1%, and co-doped $Sn_2P_2S_6$:Sb:Te 0.5%, Sb 0.5% samples. Well below the saturation level, the light induced absorption increases linearly with the intensity of pre-illumination; the overall effect becomes weaker with an increasing wavelength of pre-illumination. A typical lifetime of the secondary photorefractive centers does not depend on the preillumination light wavelength and falls into a range from 10 to 20 s for different samples and for different wavelengths of preillumination. The characteristic decay time of the defect centers responsible for photoinduced absorption is much smaller at ambient temperature for pre-illumination with green light. While the reliable data for other pre-illumination wavelengths are not available at present, it is clear that the photoinduced absorption always decays faster than the secondary photorefractive centers. From these findings it is concluded that the time delayed photoinduced absorption and photoinduced sensitizing in $Sn_2P_2S_6$:Sb develop due to at least two different types of defect centers.

The detailed description of the experiments with cw pre-illumination is given in [3]. Figure 1 shows a representative example of the temporal variation of sample transmission for a He-Ne laser probe beam. The points A and B mark the moments when green light is switched on and off, respectively. A weak probe beam illuminates the sample well before t = 0, and its intensity is partially reduced because of regular beam fanning; this steady-state value of intensity is taken as a reference level I_{pr} = 1.0. After the onset of the pre-illumination beam, the sample transmission drops dramatically. A very fast (within a fraction of second) initial decay is followed by a much slower process that saturates approximately in one minute. When the green beam is switched off, the light induced absorption starts to decay rapidly. The transmitted intensity does not immediately return to its reference level I_{pr} = 1.0, because of a strong light induced scattering (beam fanning) that develops and leads to a new (transient) depletion of the red probe beam [2,3]. Finally, all processes of population redistribution among the levels of various defect centers terminate, and the sample returns to its initial state with the transmission I_{pr} = 1.0. C, D, and E represent the points of partial decay of extinction, strongest nonlinear scattering, and recovery to the initial transmission, respectively.

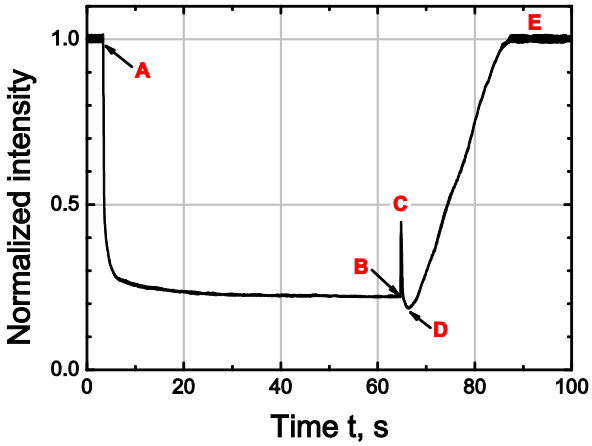

Figure 1 Temporal variation of the red testing beam intensity in response to green lightexposure for a 2mm-thick sample of $Sn_2P_2S_6$:Sb 1%.The intensity of the red probe beam is 55 mW/cm^2, while the intensity of the green auxiliary beam is 3 kW/cm^2.

In this study, we deliberately used a ns pulse pre-exposure to detect the possible sequence of processes related to the appearance of an increased effective trap density in SPS:Sb with better temporal resolution. A frequency tunable OPO (Panther EX) pumped with the third harmonic of a Q-switched Nd^{3+}:YAG (Continuum) laser was used as a pre-illumination source, while a cw 633 nm diode laser (DL633-025) served as a probe. Figure 2 shows the temporal dynamics of a 2 mm-thick $Sn_2P_2S_6$:Sb 1% sample transmission within the range of time variation that covers 10 orders of magnitude after the beginning of pre-exposure. Four processes, well separated in time, have been revealed: (i) monotonic increase of the sample absorption during the entire time of pre-exposure (≈ 15 ns pulse), i.e., formation of the first maximum of extinction, (ii) complete decay of the initial nonlinear absorption and even a partial sample "bleaching" within the time up to ≈ 1-2 ms after pre-illumination, (iii) development of the second maximum of extinction within the time interval ≈2-60 ms, and (iv) return of the sample transmission to its steady-state value within a fraction of a second.

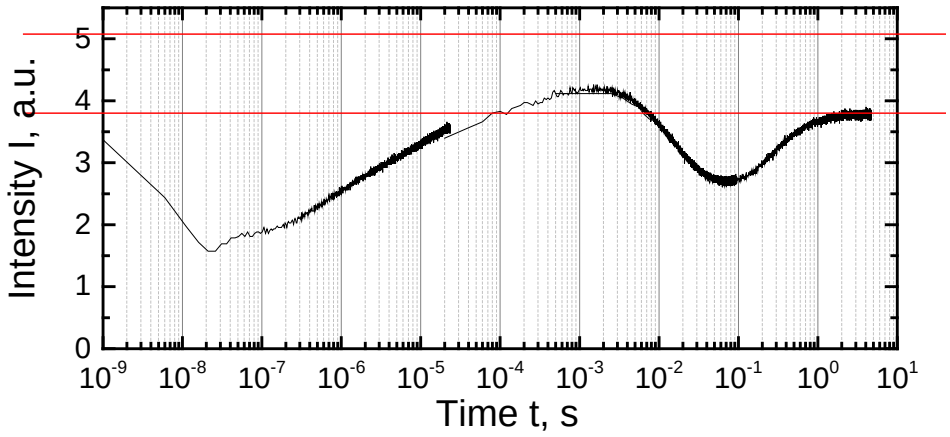

Figure 2. Temporal variation of the cw probe beam (633 nm) intensity transmitted through the $Sn_2P_2S_6$ sample during and after pre-illumination with 15 ns pump pulse (532 nm). The upper red line shows initial intensity of the probe beam, while the lower red line represents the steady-state intensity which is smaller because of partial exhaustion due to self-induced beam fanning. The intensity of the red probe beam is 0.6 W/cm^2, while the peak intensity of the green pre-exposure pulse is 3 kW/cm^2.

The contrast of the two minima in transmission follow the pre-exposure pulse intensity linearly for $I_{pulse} < 1$ kW/cm^2 and saturates for larger intensities. For large intensities, these contrasts are independent of the pre-illumination pulse polarization while they are sensitive to the probe polarization. This difference is especially large for the second extinction maximum: for probe light polarized linearly along the *x*-axis a much stronger drop of sample transmission is observed as compared to light polarized along the *y*-axis. It is established that processes (i) and (ii) are not affected by the variation of the probe beam intensity, while the time delay of second extinction maximum as well as its rise time and decay time do depend on intensity of the probe. All these particular features of the second extinction maximum suggest that the process is rather photorefractive not photochromic in nature. Fortuitously, we discovered one more argument in favor of this attribution when working in a rep. rate mode of pre-illumination, where every next green pulse entering the sample at approximately the second extinction minimum. After each pulse the sample transmission jumped within a millisecond to the transmission level that corresponds to time delay ≈ 1 ms in Fig. 2, and then the process (iii) develops until the next pre-exposure pulse arrives. This means that green pulse erases at first the most part of the light induced scattering and triggers simultaneously a normal sequence of processes shown in Fig. 2. In time traces of transmission dynamics that include several consecutive green pulses a limited temporal resolution does not allow for observing fast process (i) but process (ii) and (iii) are seen quite well.

The measurements like that shown in Fig. 2 have also been conducted with a nominally undoped $Sn_2P_2S_6$ sample. They showed a similar behavior with the formation of the light induced absorption during the pre-illumination pulse, and a subsequent return of transmission to its initial level after 10^{-3} s; however, no other minima are observed for longer observation times. This qualitative difference might suggest a conclusion that the short-living centers responsible for the first minimum of light induced absorption are the intrinsic defect centers of the crystal itself, while longer living centers responsible for the second minimum of transmission in Fig. 2 are related to the antimony doping. The second conclusion is in line with our published data on the identification of secondary centers in $Sn_2P_2S_6$:Sb using the EPR technique [4]. Recently identified intrinsic small polarons (Sn^{3+} ions) in $Sn_2P_2S_6$ crystals with a very small (<100 meV) activation energy [5] are reasonable candidates for being responsible for the fast light-induced absorption.

Finally, a comparison of cw and ns pulse pre-exposure techniques allow for concluding that the cw pre-illumination method is much more efficient for the generation of a sufficient effective trap density and thus for optical sensitizing of photorefraction in antimony doped $Sn_2P_2S_6$ crystals.

AKNOWLEDGMENTS

The financial support of the European Office of Research and Development (EOARD) via Science and Technology Center of Ukraine (STCU Grant P585) is gratefully acknowledged.

REFERENCES

[1] Pierre Mathey, Grégory Gadret, Alexander Grabar, Ivan Stoika, Yulian Vysochanskii "Photorefractive and photochromic effects in $Sn_2P_2S_6$ at various temperatures," Optics Commun., **300**, 90-95 (2013).

[2] D. Evans, A. Shuymelyuk, G. Cook, S. Odoulov, "Secondary photorefractive centers in $Sn_2P_2S_6$:Sb crystals," Optics Letters, **36**, 4, 454-456 (2011).

[3] Y. Skrypka, A. Shumelyuk, S. Odoulov, S. Basun, and D. Evans, "Light induced absorption and optical sensitizing of $Sn_2P_2S_6$:Sb," submitted for publication.

[4] A. T. Brant, L. E. Halliburton, S. A. Basun, A. A. Grabar, S. G. Odoulov, A. Shumelyuk, N. C. Giles, D. R. Evans, "Photoinduced EPR study of Sb^{2+} ions in photorefractive $Sn_2P_2S_6$ crystals," Physical Review B, **86**, 134109 (2012).

[5] A. T. Brant, L. E. Halliburton, N. C. Giles, S. A. Basun, A. A. Grabar, D. R. Evans, "Intrinsic small polarons (Sn^{3+} ions) in photorefractive $Sn_2P_2S_6$ crystals," J. Phys.: Condens. Matter, **25**, 205501 (2013).